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Tp*Cu(I)–CN–SiL$_2$–NC–Cu(I)Tp* – a hexacoordinate Si-complex as connector for redox active metals *via* π-conjugated ligands†‡

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Hexacoordinate silicon complexes L_2SiX_2 (L = a 2-benzoylpyrrol-1-yl derivative, X = CN, NCS) were synthesized from L_2SiCl_2 by ligand exchange with trimethylsilyl reagents Me_3SiX. In the presence of [Tp*CuNCMe] and Me_3SiCN the silicon complex $L_2Si(NC(CuTp^*))_2$ was obtained, which contains a linear Cu–CN–Si–NC–Cu unit (Tp* = hydrotris(3,5-dimethylpyrazolyl)borato).

There is considerable interest in the creation and exploration of metal complexes with long-range intramolecular electronic communication.[1,2] Compounds such as Prussian Blue[3] or the Creutz–Taube salt,[4] compounds with C/N ligand backbones (cyanide and pyrazine, respectively) served as early motivators. Further explorations of oligonuclear complexes with intramolecular communication between the metal atoms included carbon based bridging ligands such as (hetero)arenediyl groups and polyynes (*e.g.*, in **I**[1a] and **II**,[1b] Scheme 1). Hypercoordinate silicon chemistry, *i.e.*, the chemistry of silicon compounds with Si coordination numbers greater than four, is another field of coordination chemistry which attracts the interest of various chemists.[5,6] In this context, we reported electronic communication *via trans*-disposed ligand sites in hexacoordinate silicon complexes (*e.g.*, **III**, Scheme 1), that is, inter-ligand charge-transfer between an electron rich amido ligand and an imine moiety as electron acceptor through the near linear N–Si–N moiety.[7] Hence, hexacoordinate silicon complexes with suitable ambidentate ligands (*e.g.*, C,N based ligands with conjugated π-systems) should represent another class of potential linkers for oligonuclear metal complexes which show intramolecular electronic communication. Thus, for further studies of electronic communication *via trans*-ligands in silicon complexes we strived for creating redox-active silicon-bridged dimetallic complexes. Only few hexacoordinate Si complexes with ligand bridges to transition metals (TM) have been reported so far (*e.g.*, **IV**[8] and **V**[9]). Whereas **IV** combines more than just two transition metals in this complex (and thus has metal–ligand–Si–ligand–metal connections in both *trans* and *cis* fashion), the compounds with exclusive *trans* connections published so far (like **V** and others with Si–O–[spacer]–TM connection[10–12]) seem less likely of connecting the metal atoms *via* π-conjugation. In the particular example of **V** the authors reported cyclovoltammetric features characteristic of ferrocenecarboxylate (1 peak) and the macrocyclic ligand (3 peaks) but none of a novel "Fe_2" redox system in this complex.

Our recently reported Si-complexes with 2-benzoylpyrrolyl scaffold offered ideal prerequisites with the tendency of forming all-*trans* complexes of the type $L_2SiX'_2$ (L = 2-benzoylpyrrol-1-yl, X'_2 = Cl_2, $(OTf)_2$, ClPh).[13] Thus, we started introducing metal complexes into the Si coordination sphere of this type of complexes *via* Si–N coordination.

Out of this series, the chloro complex **1** (Scheme 2, ^{29}Si CP/MAS NMR $\delta = -171.0$ ppm)[13] was chosen as starting material for ligand exchange with Me_3SiX (X = CN, NCS). These reagents, which already have proven to be suitable cyano and thiocyanato synthons in hypercoordinate silicon chemistry,[14,15] afforded the desired complexes **2** and **3** (Scheme 2, ^{29}Si CP/MAS NMR $\delta = -198.4$ and -194.0 ppm, respectively). Their molecular structures, confirmed by single-crystal X-ray diffraction, reveal the target configuration all-*trans* (Fig. 1). In accord with findings of other groups, the cyanide in **2** is C-bound and the thiocyanate in **3** exhibits Si–N coordination.[14,15]

Cyanide and thiocyanate are known to behave as ambidentate ligands[16,17] and might thus give rise to possible coordination isomerism. Whereas the Si-bound thiocyanate already

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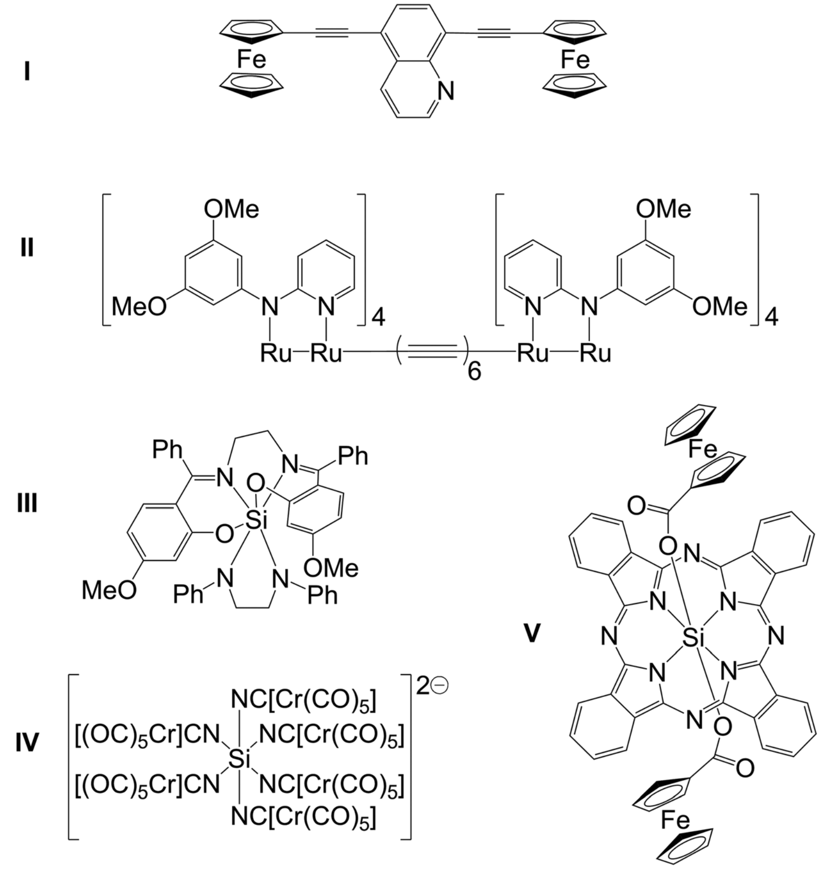
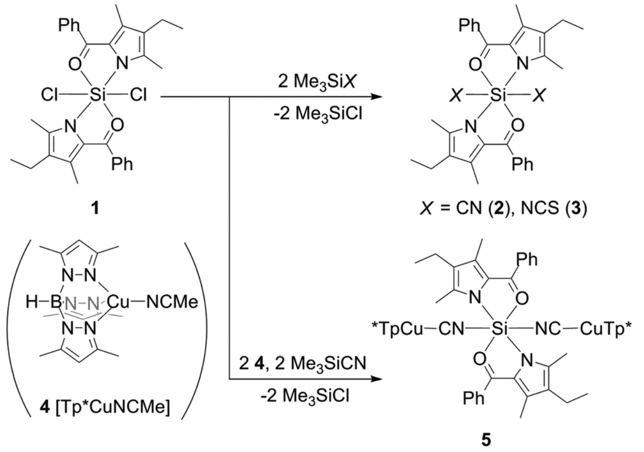
† Dedicated to Prof. Gerhard Roewer on the occasion of his 75th birthday.

‡ Electronic supplementary information (ESI) available: Cartesian coordinates and energies of the optimized molecular structures of the isomers of **2** listed in Table 1 and of all-*trans* $\mathbf{3}^{NCS}$ and $\mathbf{3}^{SCN}$, graphical representations and energies of the higest occupied MOs calculated for **5′**, CV traces of [Tp*Cu(NCMe)], [Tp*$_2$Cu] and **5**, tables with parameters of data collection and structure refinement of the crystal structures reported in this paper and CIF. CCDC 999708 (**2**·$(CHCl_3)_2$), 999703 (**3**), 999704 (**4**·MeCN), 999705 (**5**·(ferrocene)$_2$), 999706 (**5**·toluene) and 999707 (**5**·(toluene)$_4$). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt03903c



Scheme 1 Selected hexacoordinate Si complexes.



Scheme 2 Syntheses of compounds **2**, **3** and **5**.

exhibits the soft sulphur atom as a terminal group, suitable for binding to a soft transition metal atom, the cyanide in **2** binds to silicon *via* the rather soft C atom, a coordination mode which might switch to the alternative Si–N coordination as soon as a soft competitor Lewis acid is available. Thus, we analysed the alternative Si–C and Si–N coordination modes of the different octahedral isomers of **2** by quantum chemical calculations (Table 1).

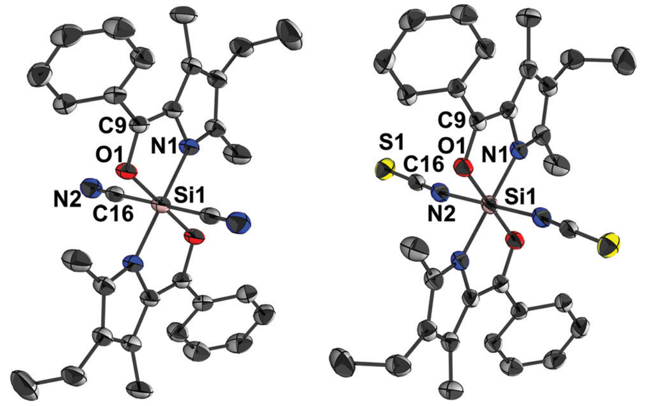


Fig. 1 Molecular structures of (from left) **2** (in **2**·$(CHCl_3)_2$) and **3** in the crystal (selected atoms are labelled, displacement ellipsoids show 50% probability, H atoms are omitted for clarity). In both cases the asymmetric unit consists of half a formula moiety, Si1 is located on a centre of inversion. Selected bond lengths [Å] and angles [°] for **2**: Si1–O1 1.779(1), Si1–N1 1.877(2), Si1–C16 1.963(2), N2–C16 1.138(3); Si1–C16–N2 176.8(2); for **3**: Si1–O1 1.766(1), Si1–N1 1.861(1), Si1–N2 1.859(1), N2–C16 1.163(2); S1–C16–N2 179.2(2), Si1–N2–C16 167.0(1).

They confirmed the experimentally encountered all-*trans* coordination with Si–C bound cyanide as an energetically favourable isomer (although only slightly lower in energy than the *N*,*N*-*trans*, *O*,*O*-*trans* and all-*cis* isomers), but the alternative

Table 1 Relative energies (kcal mol^{-1}) of isomers of $\mathbf{2^{CN}}$ and $\mathbf{2^{NC}}$ calculated with MPW1PW91/6-311G(d,p) and MP2/6-31G(d) (MP2 results are reported in parentheses)

	2^{CN}	2^{NC}
all-*trans*	0.0 (0.1)	7.0 (11.6)
X,X-trans	10.5 (8.6)	17.9 (20.6)
N,N-trans	0.1 (0.3)	7.0 (12.0)
O,O-trans	2.8 (0.4)	9.4 (11.9)
all-*cis*	1.9 (0.0)	8.7 (11.7)

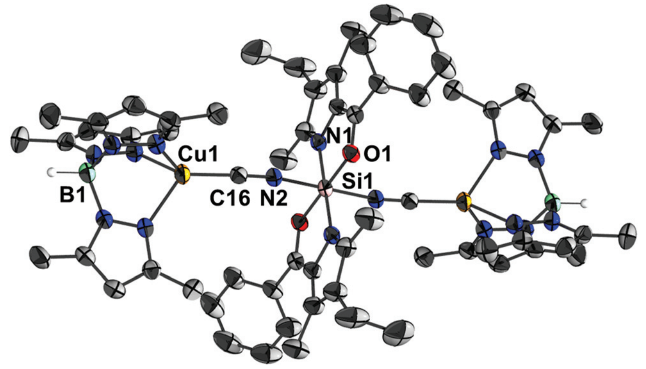


Fig. 2 Molecular structure of **5** in the crystal of **5**·(toluene)$_4$ (selected atoms are labelled, displacement ellipsoids show 30% probability, H atoms are omitted for clarity). The asymmetric unit consists of a half formula moiety, Si1 is located on a centre of inversion. Selected bond lengths [Å] and angles [°]: Cu1–C16 1.835(2), Si1–O1 1.782(1), Si1–N1 1.866(2), Si1–N2 1.848(2), N2–C16 1.157(3); Cu1–C16–N2 177.1(2), Si1–N2–C16 168.3(2).

silyl isonitrile ($\mathbf{2^{NC}}$) should be considerably less stable than the corresponding silyl cyanide complex ($\mathbf{2^{CN}}$) in all cases. For the all-*trans* isomers of **3** chosen as a representative example (*i.e.*, $\mathbf{3^{NCS}}$ and $\mathbf{3^{SCN}}$) total energy differences of 35.0/25.0 kcal mol^{-1} (DFT/MP2, same methods and basis sets used as for the isomers of **2**) were calculated, thus highlighting the pronounced stability of $\mathbf{3^{NCS}}$ over $\mathbf{3^{SCN}}$.

For further functionalisation of compounds **2** and **3** we considered tris(3,5-dimethylpyrazolyl)borato-Cu(I) (Tp*Cu) a suitable moiety which comprises an in general redox active soft metal centre within a stable coordinative scaffold with one vacant site, which can be occupied either by a neutral ligand (solvent) or alternatively by the dangling donor atoms of the ambidentate ligands in **2** and **3**. Thus, complex [Tp*Cu-NCMe] (**4**, Scheme 2) with the labile acetonitrile ligand[18] should serve as a convenient precursor (for its crystallographic characterisation see the ESI‡). Comparative cyclovoltammetric measurements on [Tp*Cu-NCMe] and on the corresponding Cu(II) complex [Tp*$_2$Cu][19] have shown that [Tp*Cu-NCMe] undergoes irreversible oxidation and reduction processes in the range between −1.0 and +1.0 V. Thus, the CV features of [Tp*Cu-NCMe] are different from the cyclovoltammetric behaviour of [Tp*$_2$Cu], which does not reveal any striking redox chemistry in the range between −2.0 and +2.0 V (for CV traces see the ESI‡). We attribute the irreversible nature of the CV characteristics of [Tp*Cu-NCMe] to the labile MeCN ligand, which might turn into reversible redox features upon introducing a less labile ligand.

For complex **3** reaction with **4**·MeCN failed. Both the treatment of **3** with this copper(I) complex and the one-pot reaction of **1** and Me_3SiNCS in the presence of **4**·MeCN only afforded compound **3**.

In contrast, the analogous one-pot reaction of **1**, **4**·MeCN and Me_3SiCN led to the formation of complex **5** (Scheme 2). This compound reveals much better solubility in organic solvents and its formation was first indicated by a ^{29}Si NMR signal at −197.6 ppm in toluene. Crystallisation from toluene eventually afforded single-crystals suitable for X-ray diffraction analysis (Fig. 2). Although two solvates were obtained, *i.e.*, **5**·(toluene)$_4$ and **5**·(toluene) (and a ferrocene solvate had also been obtained, *vide infra*), in all of them the molecular structure of **5** exhibits an octahedrally all-*trans* coordinated Si atom in an almost linear Cu–CN–Si–NC–Cu sequence. Crystal packing effects lead to some variations in the Si–N–C (168.3(2)–174.7(3)°) and Cu–C–N angles (171.9(2)–177.1(2)°), whereas Si–N (1.841(4)–1.866(2) Å) and Cu–C bond lengths (1.829(5)–1.851(2) Å) are very similar and C–N bond lengths (1.157(3)–1.163(5) Å) are basically identical within this set of crystallographically characterised related molecular structures.

To the best of our knowledge compound **5** is the first hexacoordinate silicon complex which holds two electron rich and redox active metal atoms connected *via* bridging ligands L′ capable of π-conjugation. Only two further examples of crystallographically characterised complexes of the type *trans*-M–CN–MM6–NC–M (where M is any metal and MM6 is a hexacoordinate group 14 metal or metalloid atom)[20] were found in the literature, one of them being complex **IV**[8] and the other one the trinuclear complex $\{[(PhO)_3P](dppm)(CO)_2Mn\text{-}CN\}_2SnCl_4$ (**VI**), where dppm = bis(diphenylphosphino)methane.[21] Related structures for MM6 being a hexacoordinate group 13 or group 15 element have not been found.[20] The C–N bond lengths in **IV** and **VI** are the same as in **5** (in both compounds 1.16 Å within the standard deviation). Furthermore, in **IV** the Si–N bond lengths (1.80–1.83 Å) are only slightly shorter than those in **5** and Si–N–C angles (169–177°) are variable within the same range. With respect to other hexacoordinate silicon complexes which contain the Si6–N2–C2–X moiety (*i.e.*, containing two-coordinate N and C atom), derivatives with X = O (13 hits), S (19 hits), Se (1 hit) were found.[20] The Si–N bond lengths cover the ranges of 1.78[22]–1.85[23] Å (for X = O), 1.81[15a]–1.97[24] Å (for X = S) and 1.89 Å (for X = Se[25]). The very long Si–NCS bond of 1.97 Å[24] is caused by the influence of the electron releasing *trans*-substituent, *i.e.*, a methyl group. This set of structures of Si6–N2–C2–X compounds reveals even greater variability of the Si–N–C angles, which cover the ranges of 180–146°[26] (X = O), 180–151°[24] (X = S) and 176° (X = Se[25]).

In order to elucidate the electronic communication between the two Cu-centres in complex **5** that are formally connected by a five atom C–N–Si–N–C "wire" we performed quantum chemical calculations on a simplified model complex **5′** (with all alkyl substituents replaced by hydrogens). The highest occupied molecular orbitals (in particular HOMO,

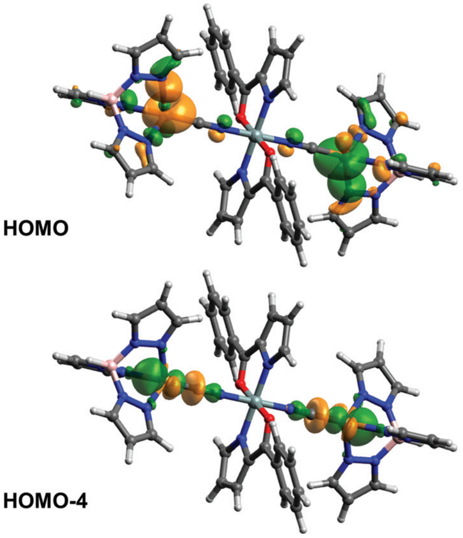


Fig. 3 HOMO and HOMO−4 calculated for **5′**.

−1, −2, −3, −4, −5, −8, −9, −10, −11) are located at both Cu atoms and their ligand atoms with equal orbital contributions, as shown for HOMO and HOMO−4 as representative examples (Fig. 3), *i.e.*, they are indeed delocalised about the Cu–CN–Si–NC–Cu axis. To confirm this communication between the copper atoms in **5** experimentally, we aimed at generating a compound 5^+ with mixed oxidation states at the copper atoms, *i.e.* Cu(I)/Cu(II). On a synthetic route we thus applied ferrocenium hexafluorophosphate ($FcPF_6$, Fc^+ as oxidant)[27] in an equimolar ratio.

Unfortunately, we only were able to isolate some crystals of a co-crystallisate of **5** with two equivalents of ferrocene instead of the desired compound and without any hints at the fate of the potential reducing agent. Apparently, one fraction of the starting material **5** must have reacted with Fc^+ in a 2 : 1 molar ratio, and the other fraction remained intact and thus available for co-crystallisation with the ferrocene formed. For *in situ* monitoring of the redox process we therefore applied cyclic voltammetry (CV) to an acetonitrile solution of 10^{-4} M **5** (Bu_4NPF_6 0.1 M). The CV features of [Tp*CuNCMe] (in the range between −0.5 and +0.5 V) are absent, instead we found an irreversible process at +1.1 V. This shift of the first oxidative process to more positive potential strongly hints at the stabilisation of Cu(I) in complex **5** and, together with the irreversibility of this redox step, at the instability of a hypothetical monocationic complex 5^+. Even though tetrahedral coordination is frequently encountered with both Cu(I) and Cu(II), the degenerate orbital situation associated with complex **5** and the degenerate SOMO resulting therefrom in case of formation of a Cu(I)/Cu(II) complex 5^+ apparently gives rise to the more positive oxidation potential and supports decomposition upon oxidation.

Conclusions

Ligand exchange between trimethylsilyl cyanide and complex **1** (L_2SiCl_2, L = O,N bidentate ligand) in the presence of the Cu(I) complex **4** (Tp*CuNCMe) furnished the hexacoordinate silicon complex **5** with an almost linear Cu–C–N–Si–N–C–Cu sequence. Although electronic communication is evident from the delocalisation of MOs about the two Cu atoms, attempts at one-electron-oxidising this "Cu_2 entity" failed with decomposition of the oxidation product. In principle, our synthetic approach is promising for the generation of further oligonuclear complexes with linear M–C–N–Si–N–C–M sequence for further investigations of redox, electronic, magnetic and related properties.

Experimental – general considerations

All manipulations were carried out using standard Schlenk and Glovebox techniques under an atmosphere of dry argon. Compound **1** (L_2SiCl_2) was prepared as reported earlier.[13] Acetonitrile was purchased from Roth in an Ultra LC-MS grade quality (99.98%) and stored over activated molecular sieves 3 Å. Toluene was distilled from sodium and stored over sodium wire. $CDCl_3$ was purchased from Armar Chemicals and stored over activated molecular sieves 3 Å. Potassium hydrotris(3,5-dimethylpyrazolyl)borate (KTp*) and CuCl were prepared according to established methods.[28,29] Trimethylsilylcyanide was purchased from Aldrich and used without further purification. Trimethylsilylthiocyanate was prepared from dry NaNCS and chlorotrimethylsilane in a modified procedure related to an earlier report.[30] Ferrocenium hexafluorophosphate ($FcPF_6$) was prepared according to a literature procedure.[27]

Quantum Chemical calculations were carried out using the Gaussian09 package.[31] Molecules were optimized at the DFT MPW1PW91/6-311G(d,p) level of theory. Additional single point energy calculations for the optimized structures were performed at the MP2/6-31G(d) level. For compound **5′** population analyses were carried out after optimization using DFT MPW1PW91/6-311G(d,p) for the s and p block elements and a Stuttgart–Dresden effective core potential (SDD) for the copper atoms.

Elemental analyses were carried out with a Vario Micro Cube analyser (Elementar, Hanau, Germany). ^1H, ^{11}B, ^{13}C and ^{29}Si NMR spectra were recorded on a Bruker DPX 400 spectrometer or on a Bruker AVANCE 500 spectrometer. Chemical shifts are given in ppm relative to $SiMe_4$ (as internal standard for ^1H, ^{13}C and ^{29}Si) or $BF_3 \cdot Et_2O$ (externally referenced for ^{11}B). ^{29}Si CP/MAS NMR spectra were recorded on a Bruker Avance 400 WB spectrometer (using a 4 mm ZrO_2 rotor or a 7 mm ZrO_2 rotor with KelF insert) and referenced against external Q_8M_8 (−109 ppm for the most upfield peak).

X-ray crystallography

Single-crystal X-ray diffraction data were collected on a Stoe IPDS-2/2 T diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Crystals were selected under an inert oil and mounted on a glass capillary which was coated with a thin layer of silicone grease. The structures were solved by direct methods (Shelxs-97)[32,33] and refined with full-matrix least-squares methods (refinement of F^2 against all reflections with Shelxl-97).[33,34] All non-hydrogen atoms were refined anisotropically. C bound H-atoms were refined in idealised positions, the coordinates of the BH-hydrogen atoms were refined isotropically without restraints. For the cyanosilicon compounds **2**·$(CHCl_3)_2$ and **5**·(toluene) we have probed the Si–C (in **2**) and Si–N coordination mode (in **5**) by a test refinement of the cyano moiety (C16–N2) together with an alternative moiety of inverted atomic sites (N2a–C16a), same coordinates and anisotropic displacement parameters for C16 and N2a, N2 and C16a, and a free variable for the site occupancy with the alternative orientations of the CN moiety. We found, within the 3-fold standard deviation, full site occupancies for the herein reported coordination modes (0.94(3) of Si–CN in **2** and 0.99(5) Si–NC in **5**).

Syntheses and characterisation

$L_2Si(CN)_2$ (2). Trimethylsilylcyanide (150 mg, 1.50 mmol) was added to a suspension of **1** (275 mg, 0.50 mmol) in MeCN (25 mL) and the mixture was stirred at 80 °C for 7 h. After cooling to room temperature the yellow solid was collected by filtration, washed with MeCN (2 × 1 mL) and dried *in vacuo*. Yield 174 mg (0.33 mmol, 65%).

^{1}H NMR (500 MHz, 40 °C, $CDCl_3$): δ 1.10 (t, ^3J(H,H) = 7.5 Hz, 6H, CH_2CH_3), 2.13 (s, 6H, CH_3), 2.45 (q, ^3J(H,H) = 7.5 Hz, 4H, CH_2CH_3), 2.68 (s, 6H, CH_3), 7.53–7.56 (m, 4H, *m*-Ph), 7.60–7.63 (m, 2H, *p*-Ph), 7.84–7.86 (m, 4H, *o*-Ph). ^{13}C NMR (125 MHz, 40 °C, $CDCl_3$): δ 12.4, 14.0, 14.2 (CH_3), 17.9 (CH_2), 128.5, 129.7 (*o*/*m*-Ph), 132.4 (*p*-Ph), 132.3, 133.7, 136.2, 138.6, 157.1 (i-Ph, pyr), 135.2 (CN), 169.4 (CO); ^{29}Si NMR (99.4 MHz, 40 °C, $CDCl_3$): δ −199.5.

^{29}Si CP/MAS NMR (79.5 MHz, ν_{spin} = 4 kHz): δ_{iso} −198.4.

C/H/N microanalysis calcd (%) for $C_{32}H_{32}N_4O_2Si$: C 72.15, H 6.05, N 10.52; found: C 71.98, H 6.13, N 10.22.

A sample (*ca.* 20 mg) of **2** was dissolved in a mixture of chloroform (4 mL)–toluene (1 mL) upon heating. Storage at −24 °C afforded crystals of **2**·$(CHCl_3)_2$ suitable for X-ray diffraction analysis.

$L_2Si(NCS)_2$ (3). Trimethylsilylthiocyanate (100 mg, 0.75 mmol) was added to a suspension of **1** (140 mg, 0.25 mmol) in MeCN (20 mL) and the mixture was stirred under reflux for 2 h. Upon addition of further MeCN (25 mL) while refluxing a clear solution was obtained. Cooling to room temperature and storage overnight afforded yellow crystals of **3** suitable for X-ray diffraction analysis. The solid was separated from the mixture by decantation, washed with MeCN (2 × 1 mL) and dried *in vacuo*. Yield 90 mg (0.15 mmol, 59%).

^{1}H NMR (500 MHz, 40 °C, $CDCl_3$): δ 1.11 (t, ^3J(H,H) = 7.7 Hz, 6H, CH_2CH_3), 2.11 (s, 6H, CH_3), 2.44 (q, ^3J(H,H) = 7.7 Hz, 4H, CH_2CH_3), 2.63 (s, 6H, CH_3), 7.53–7.56 (m, 4H, *m*-Ph), 7.60–7.63 (m, 2H, *p*-Ph), 7.82–7.83 (m, 4H, *o*-Ph). ^{13}C NMR (125 MHz, 40 °C, $CDCl_3$): δ 12.4, 14.0, 14.2 (CH_3), 17.9 (CH_2), 128.6, 129.8 (*o*/*m*-Ph), 132.4 (*p*-Ph), 129.4, 132.1, 135.8, 138.1, 157.2 (i-Ph, pyr), 169.2 (CO), resonance signal for S*C*N not observed; δ ^{29}Si signal not observed due to poor solubility.

^{29}Si CP/MAS NMR (79.5 MHz, ν_{spin} = 4 kHz): δ_{iso} −192.1.

C/H/N microanalysis calcd (%) for $C_{32}H_{32}N_4O_2SiS_2$: C 64.40, H 5.40, N 9.39; found: C 64.14, H 5.39, N 9.43.

Tp*Cu(NCMe)·MeCN (4·MeCN). A suspension of KTp* (3.36 g, 10.0 mmol) in MeCN (80 mL) was added to a solution of CuCl (990 mg, 10 mmol) in MeCN (20 mL) while maintaining a solution temperature of 80 °C. Thereafter the mixture was kept at 80 °C for 90 min and subsequently filtered whilst hot. The residue was washed with MeCN (5 mL). From the combined filtrate and washing a crystalline product was obtained upon cooling to room temperature. To improve the yield the mixture was stored at −24 °C overnight. One of the crystals was chosen for X-ray diffraction analysis. The mother liquor was decanted off, the white solid was washed with MeCN (2 × 1 mL) and dried *in vacuo*. Yield 2.95 g (6.70 mmol, 67%) of **4**·MeCN.

^{1}H NMR (400 MHz, 23 °C, C_6D_6): δ 0.62 (s, 6H, CH_3CN), 1.84 (s, 9H, *pz*CH_3), 1.29 (s, 9H, *pz*CH_3), 5.76 (s, 3H, *pz*H), ~4.9 (very broad, 1H, HB*pz*$_3$); ^{13}C NMR (100.1 MHz, 23 °C, C_6D_6): δ 0.11 (CH_3CN), 13.6 (*pz*CH_3), 13.8 (*pz*CH_3), 105.4 (4-*pz*), 116.0 (CH_3CN), 144.9, 148.7 (3,5-*pz*).

C/H/N microanalysis calcd (%) for $C_{19}H_{28}BN_8Cu$: C 48.46, H 5.99, N 23.79; found: C 48.73, H 6.31, N 23.60.

$L_2Si(NC\text{-}CuTp^*)_2$ (5). Trimethylsilylcyanide (75 mg, 0.75 mmol) was added to a suspension of **4**·MeCN (222 mg, 0.5 mmol) and **1** (140 mg, 0.25 mmol) in toluene (2.5 mL) at 60 °C. After stirring at 60 °C for 30 min the slightly turbid mixture was filtered (without washing) and the filtrate was stored at room temperature without any disturbance. After storage overnight a yellow crystalline material was obtained. The crystals were suitable for X-ray diffraction analysis. The solid product was isolated by decantation, washed with toluene (1 mL) and dried *in vacuo*. Yield 90 mg (0.06 mmol, 25%) of **5**·toluene.

^{1}H NMR (500 MHz, 23 °C, $CDCl_3$): δ 1.10 (t, ^3J(H,H) = 7.4 Hz, 6H, CH_2CH_3), 1.97 (s, 18H, pz-CH_3), 2.13 (s, 6H, pyr-CH_3), 2.24 (s, 18H, pz-CH_3), 2.46 (q, ^3J(H,H) = 7.4 Hz, 4H, CH_2CH_3), 2.69 (s, 6H, pyr-CH_3), ~4.5 (s, very broad, 2H, B-H), 5.51 (s, 6H, pz-H) 7.52–7.55 (m, 4H, *m*-Ph), 7.60–7.63 (m, 2H, *p*-Ph), 7.82–7.83 (m, 4H, *o*-Ph). ^{13}C NMR (125 MHz, 23 °C, $CDCl_3$): δ 12.3 (pyr-alkyl), 12.4 (pz-CH_3), 13.5 (pz-CH_3), 13.8, 14.3, 17.8 (pyr-alkyl), 103.7 (pz-*C*H), 128.5 *o*/*m*-Ph, 129.4 (*o*/*m*-Ph), 132.2, 132.2, 132.3 (*o*-,i-Ph, pyr), 133.0, 135.7 (pyr), 142.4, 146.7 (pz), 157.0 (pyr), 169.3 (CO) resonance signal for *C*N not observed; ^{11}B NMR (160.4 MHz, 23 °C, $CDCl_3$): δ −9.8 (br); ^{29}Si NMR (99.4 MHz, 23 °C, $CDCl_3$): δ −197.9.

^{29}Si CP/MAS NMR (79.5 MHz, ν_{spin} = 5 kHz): δ_{iso} −197.5.

C/H/N microanalysis calcd (%) for $C_{62}H_{76}B_2Cu_2N_{16}O_2Si\cdot C_7H_8$: C 61.56, H 6.29, N 16.65; found: C 61.27, H 6.58, N 16.98.

Storage of the supernatant at −24 °C afforded further crystals, this time of the composition **5**·$(toluene)_4$, which dissolved upon removal from the freezer.

Reaction of 5 with ferrocenium hexafluorophosphate ($FcPF_6$). **5**·toluene (125 mg, 0.10 mmol) and $FcPF_6$ (33 mg, 0.10 mmol) were dissolved in dichloromethane (1.5 mL) and the resulting clear solution was stirred for 5 min. Upon diffusion of pentane into the mixture at ambient temperature a dark solid was obtained containing crystalline material suitable for X-ray diffraction analysis, which revealed the structure of **5**·(ferrocene)$_2$. The identity of any obligatory oxidation product could not be elucidated.

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